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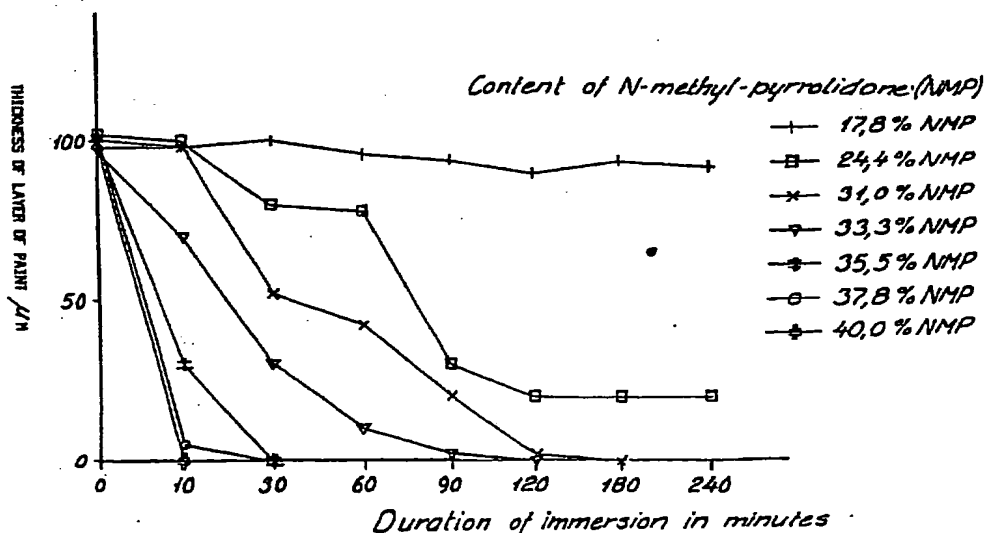
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/DK92/00331 (22) International Filing Date: 11 November 1992 (11.11.92) (30) Priority data: 1854/91 12 November 1991 (12.11.91) DK (71)(72) Applicant and Inventor: LARSEN, Ebbe, Damgaard [DK/DK]; Søndermarksvej 4, DK-2630 Taastrup (DK). (74) Agents: SCHØNNING, Søren et al.; International Patent- Bureau, Høje Taastrup Boulevard 123, DK-2630 Taa- strup (DK). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CS, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, PL, RO, RU, SD, SE, UA, US, Eu- ropean patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).		Published With international search report. In English translation (filed in Danish).

(54) Title: COMPOSITION FOR STRIPPING ENAMELED OR PAINTED SURFACES AND METHOD FOR ITS MANUFACTURE



(57) Abstract

An essentially anhydrous composition for stripping objects of materials vulnerable to corrosion, said composition containing N-methyl-pyrrolidone, potassium hydroxide and an alcohol having 2-3 carbon atoms, contains said components in the following amounts: A) 0-3 % by weight of water, B) 0.05-10 % by weight of potassium hydroxide, C) 35-90 % by weight of N-methyl-pyrrolidone, and D) 10-60 % by weight of an alcohol chosen among ethanol, n-propanol and i-propanol or mixtures thereof. In this way a stripping composition is provided, which is capable of dissolving a considerable number of commonly used types of enamel, which does not corrode aluminium and which does not present any danger to the health of the persons using the composition.

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COMPOSITION FOR STRIPPING ENAMELED OR PAINTED SURFACES AND
METHOD FOR ITS MANUFACTURE

5 The present invention relates to an essentially
anhydrous composition for coating stripping objects of
materials vulnerable to corrosion, said composition
containing N-methyl-pyrrolidone, potassium hydroxide and an
alcohol having 2 - 3 carbon atoms.

10 In industrial productions of most articles for
everyday use a high finish is a prerequisite among others in
the form of a flawless enamel coating, which moreover has to
have a shade of colour corresponding exactly to the colour
sample chosen. Does the manufactured object not meet these
15 requirements, it has to be re-enamelled, if is possible and
economically feasible, otherwise it has to be discarded. As
in particular the latter possibility is a costly solution,
great interest has been attached to making a re-enamelling
possible after removal of the first coating of paint by
20 means of a composition for dissolution and removal of the
hardened enamel.

 An enamel coating may be removed by chemical, thermal
or mechanical stripping methods. The two last-named methods
are not economical and are absolutely not applicable in
25 connection with an important material group, viz. aluminium,
which cannot stand the thermal or mechanical strain. For
chemical stripping chlorinated hydrocarbon in pure form, for
instance methylene chloride, or in admixture with other
possibly aromatic hydrocarbons, have been used as so-called
30 cold-strippers. The use of chlorinated hydrocarbons for
stripping purposes does, however, in practice present a
serious risk to the environment, as it is most difficult to
safeguard the persons, which are to work with these
solvents, and it is costly to dispose of the stripping
35 compositions after use together with the dissolved remnants
of paint. Methylene chloride is moreover aggressive towards
aluminium, which as mentioned is a frequently used material
for the production of common articles for everyday use.

From US Patent No. 3,551,204 solvents are known which are suited for selective dissolution of polyurethane and certain epoxy resin systems, but which do not attack metals or most of the remaining polymer systems. The solvents, which are used for removing encapsulations around electronic components, in such a way that the components can be recovered without damage, are mainly based on a strong, inorganic base, for instance potassium hydroxide, and an alcohol with 2-4 carbon atoms, among which alcohols isopropanol is the most preferred one. In the patent it is said that a content of 5-10% of other solvents, such as dimethylformamide, dimethylsulfoxide, methylene chloride or methyl-pyrrolidone may be added with a view to attaining an extra dissolving effect. With methyl-pyrrolidone as component the known solvent comprises the following: 0.1 - 3% by weight of water, 3 - 7% by weight of potassium hydroxide, 90 - 96.4% by weight of an alcohol with 2-3 carbon atoms, and 5 - 10% by weight of N-methyl-pyrrolidone. However, the presence of such other solvents as N-methyl-pyrrolidone influences the selectivity of the solvent, but may be used in mildly corroding solvent compositions for certain polyesters. The known solvent has a strong effect on polyurethane, which according to the described examples can be dissolved completely.

US Patent No. 3,954,648 discloses coating stripping compositions based on an alkali metal hydroxide in the amount of 0.25 - 10% by weight dissolved in a mixture of 40 - 60% by weight of an oxygenated solvent, for instance an alcohol with a boiling point temperature above 100°C, and 40 - 60% by weight of an amine with a high boiling point. Such a stripping composition based on triethylene glycol and triethanol amine is capable, when immersed for 7-30 minutes in a bath with a temperature of 130-150°C, of dissolving a broad variety of paintings and enamels to such an extent that they can be removed by rinsing with water. In the publication pyrrolidone is given as an example of a suitable amine. It is a disadvantage in the known stripping composition, which is a so-called "warm-stripper", that in

order to reach a sufficient effect it has to be heated to a temperature so high as approx. 150°C.

It is the object of the invention to provide a stripping composition or solvent which is characteristic in having a low toxicity towards the persons using it, good solubility at room temperature and to which aluminium is not vulnerable in respect of corrosion. Besides, the stripping composition is to be regeneratable, so that there will be no problems for the user in respect of discarding it.

This object is met according to the invention in that the stripping composition is characteristic by the subject matter of the characterizing clause of claim 1.

The invention is based on the realization that an alkali dissolved in common alcohol has a strongly decomposing effect on a great number of the commonly used paint systems, if the paint is effectively swelled, so that the alkali becomes able to attack the "condensation bindings" of the paint film. Such a swelling can be established by means of methyl-pyrrolidone in concentrations that are several times as big as the ones previously proposed for instance in the above US Patent No. 3,551,204. Series of tests with stripping compositions with a varying content of N-methyl-pyrrolidone show, when objects lackquered with commonly used types of enamel are stripped, that the prerequisite for the swelling effect, which is the basis for the stripping effect, to take effect immediately, is closely connected with the concentration of the methyl pyrrolidone, and that the effect does not set in until at concentrations over 35% by weight, the effect setting in then at room temperature. The composition only consists of few components, and the simple composition makes it possible to recover the stripping composition, when after use for a longer time it has lost its effectiveness, and/or to stimulate the composition during use, the effective period of use being thus considerably increased. The use of the composition is simple, the composition, which is water-soluble, being simply washed off after the stripping, and such a washing is from an environmental point of view fully

justifiable, as the components of which the stripping composition consists are decomposable in the natural cycle. By means of the invention a generally applicable stripping composition has been provided in a surprisingly simple way
5 by re-development from a known selective solvent, said composition having an exceedingly low toxicity, and by the use of which no precautions are to be taken other than those commonly recognized as necessary in the use of inflammable liquids. The composition excels in having in all essentials
10 just as strong a decomposition power at room temperature towards most paint and enamel types as the known "warm-stripper".

A preferred composition is disclosed in claim 2.

According to the invention the stripping composition
15 may be produced by the method stated in claim 4. A side effect of the method used for the manufacture of the stripping composition is that the stripping composition may be stimulated in a simple way during the use thus preserving its effect, the components to be added for the stimulation
20 just having to be added and mixed by stirring.

The stripping composition according to the invention is in particular useful for stripping of easily corrosive metals by coldstripping. The coldstripping is preferably carried out by spraying instead of by immersion. In
25 connection with the spraying the objects are subjected to an aerosol mist, whereby in comparison with the immersion both shorter stripping times and a smaller consumption of chemicals are attained.

The invention shall be described in detail in the
30 following by means of some examples and the enclosed diagram.

The stripping composition according to the invention is manufactured by adding potassium hydroxide to an ethyl alcohol possibly heated to boiling by stirring, whereafter
35 methyl-pyrrolidone is added in an amount preferably corresponding to that of the solvent.

In such a product the potassium hydroxide will only to a small extent be dissociated, and the stripping

composition will not therefore be reactive towards corrosive metals such as aluminium. The product will therefore be suited for stripping of objects of aluminium by coldstripping, i.e. by subjecting the objects to the product at room temperature, until the enamel is dissolved, whereafter the objects are taken up and rinsed by water. Though the product is thus completely mixable with water, it should not be exposed to any kind of mixing with water during use, as such a mixing even in small amounts partly will increase the degree of dissociation and thereby the risk of corrosion of aluminium, and partly increase the risk of etching the skin of the persons using the stripping composition.

Tests have been made to demonstrate the effect of N-methyl-pyrrolidone in a solution of potassium hydroxyde in ethanol. The tests were carried out with polyester-coated test sheets of aluminium, which were subjected to various liquid combinations at room temperature.

The following stripping compositions were made with the following combinations from ethanol (99.6%) (EtOH), potassium hydroxide (analysis article) (KOH) and N-methyl-pyrrolidone (technical quality) (NMP):

Test series I:

	I	II	III	IV	V	VI	VII	VIII
EtOH% by weight	90	80	60	50	40	30	20	10
NMP% by weight	8	18	38	48	58	68	78	88
KOH% by weight	2	2	2	2	2	2	2	2

Test series II:

	I	II	III	IV	V	VI
EtOH% by weight	84,21	73,68	63,16	52,63	42,11	31,58
NMP% by weight	10,53	21,05	31,58	42,11	52,63	63,16
KOH% by weight	5,26	5,26	5,26	5,26	5,26	5,26

The stripping compositions according to test series I were tested in a number of tests with polyester-coated test sheets of aluminium, which was subjected to various liquid combinations at room temperature. The test sheets were an alloy 2S(AA1200) from Hydro aluminium and chromated in accordance with RAL Std GSB 612 - yellow chromation. They were given a polyester enamel INTERPOND D86 (TGIC-hardener) from International Farvefabrik A/S in a layer of 100-120 μ m and hardened at 200°C in 10 minutes.

Liquid composition nos. I and II in test series I showed no visible decomposition of the polyester-coating after exposure in 1 hour. After exposure for 4 hours the tests showed weak signs of decomposition (crispness), but no stripping effect of the substrate, and after 13 hours the coating was still fixedly adhering to the substrate, but could be removed by heavy mechanical influence.

Composition nos. III - VIII: All coatings showed immediate tendency to dissolve after immersion for a short period (3 minutes). After 30 minutes the coatings, which had been subjected to composition nos. IV - VII, were dissolved, and the remaining coatings could be removed by rinsing with water. After 1 hour all coatings subjected to composition III - VIII were totally dissolved.

Corresponding stripping tests were carried out with the liquid composition according to test series II. Similar to test series I the polyester-coated test sheets of extruded aluminum, which had been green-chromated in accordance with DIN 50 939, were subjected to various liquid combinations at room temperature. The painting was carried out with INTERPOND 600, which is a polyester lacquer hardened with TGIC, supplied by International Farvefabrik A/S.

The tests showed that in connection with liquid composition I and II no visible decomposition could be seen after exposure for 30 minutes. The compositions II - VI were all after immersion for 30 minutes capable of performing a complete stripping, and with composition VI the stripping was attained in less than 2 minutes.

The test series show that comparatively small contents of N-methyl-pyrrolidone of approx. 20% by weight or less do not influence the solvability of an alkali dissolved in an alcohol, but that at a content of approx. 35% by weight or more a surprising improvement of the stripping ability of the mixture occurs. Furthermore, the test series show that even though the content of alkali is increased, no decisive improvement of the stripping effect is achieved in comparison with the improvement attained by high contents of N-methyl-pyrrolidone. The test series, which are carried out with typical and frequently used polyester lacquers, show that the stripping effect of the composition according to the invention matches the stripping effect of known warm-strippers.

To illucidate the efect of the content of N-methyl-pyrrolidone of the stripping composition at concentrations in the range between approx. 18 and 40% by weight further tests have been made, which support the observation of the comparatively sharp borderline for the combination effect between N-methyl-pyrrolidione and KOH dissolved in an alcohol with 2-4 carbon atoms. The result of the test series is shown in the diagram of the drawing. The diagram shows the thickness of a layer of enamel of a TGIC-hardened polyester lacquer on green-chromated aluminium after stripping for various periods of time of maximum 240 minutes. In the test the same concentration of KOH was used, viz. 2.2% by weight, while the ratio between ethyl alcohol and N-methyl-pyrrolidione was varied. In the diagram the content of N-methyl-pyrrolidone (NMP) is stated, the content of ethanol (EtOH) making up the rest to 100% by weight.

It will be seen from the diagram that with a content of NMP below 18% by weight no actual stripping is attained, and that a quick and distinct effect after 10 minutes in the bath requires a content of at least 33% by weight NMP, and it can thus be seen that with the stripping composition according to the invention a better effect is attained than with the composition disclosed in US Patent no. 3,551,204.

The test series is carried out with a commonly used

polyester lacquer, but a good effect of the stripping composition according to the invention has been found towards the following types of lacquer:

- 5 Cellulose lacquers (nitro cellulose, acetyl cellulose etc.)
- Chlorinated caoutchouc
- Polyvinyl chloride (PVC)
- Polyvinyl acetate (PVA)
- 10 Polyacryl nitril
- Polyacrylate
- Polystyrene

 However, tests have also shown that there are certain
15 types of lacquers, in connection with which the stripping composition according to the invention is not effective, and among these can be mentioned: Nylon (RILSAN), vinyl (LEVASINT), certain types of electroforese lacquers and certain epoxy lacquers.

20 Tests have likewise shown that the stripping composition becomes less active toward enamel and paint at a water content exceeding approx. 2.5%, and at the same time the composition shows an increasing tendency of being
corrosive against light-alloy metals. During the stripping
25 process OH-ions are used, and likewise a certain evaporation of the comparatively volatile alcohol will take place. Through a period of use for a bath with the stripping composition a periodic stimulation should therefore take place by admixture of a potassium-hydroxide-containing
30 alcohol.

 After a longer period of use considerable amounts of decomposed lacquer will accumulate. The content of N-methylpyrrolidone in the bath remains, however, essentially the same. It is therefore possible, instead of discarding the
35 bath, to let it regenerate. The regeneration mainly consists in a filtration, but may also consist of a proper separation of the chemicals forming part thereof, for instance by a vacuum distillation. An important prerequisite for such a

regeneration is the simple structure of the stripping composition and the method of manufacture used, which prevents a decomposition of the N-methyl-pyrrolidone.

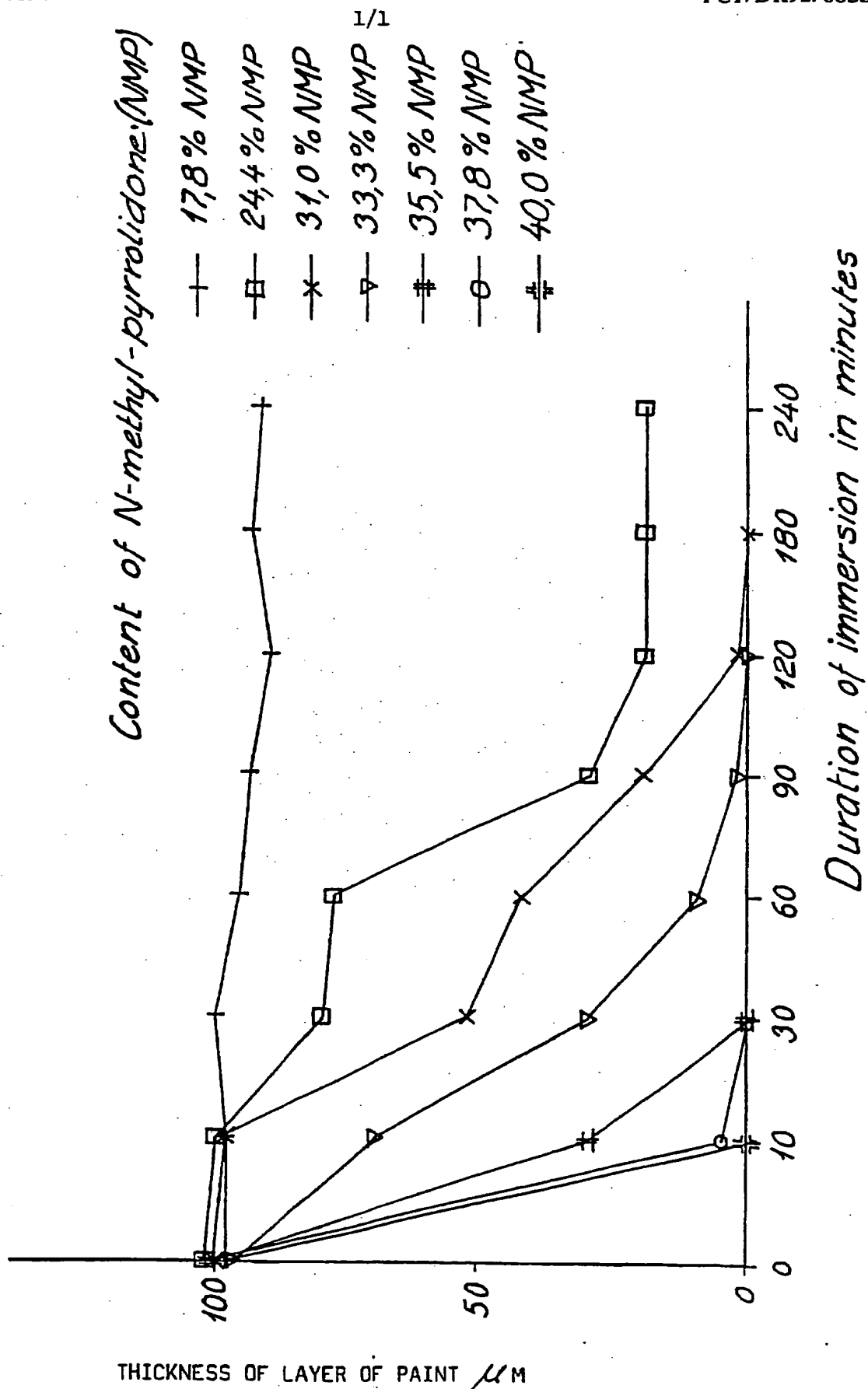
The formulation of the stripping composition has the effect that the composition gets a low flash point and therefore requires great care during use on account of danger of fire. It is possible to raise the flash point of the composition by adding a glycol, in particular butyl diglycol. Butyl diglycol is preferred on account of its commercial availability at moderate prices and the modest safeguard measures necessary for its use. With an admixture of butyldiglycol it will be possible to raise the flash point of the stripping composition to at least 21°C. The glycol has no demonstrable influence on the effect of the stripping composition, but acts as a filler in the component mixture. Only if the stripping composition is circulated by means of a pump can a certain greasing effect be seen on the movable parts of the pump. The glycol fraction will to a certain degree by a regeneration combine with the dissolved saponification residues.

It is possible completely or partly to replace the ethanole by other forms of alcohols with 2-3 carbon atoms, such as n-propanol and i-propanol.

It is also possible to add thickening means for the formation of a paste, whereby the stripping composition will also be applicable without the objects to be stripped having to be immersed in a bath of the composition.

C l a i m s

1. An essentially anhydrous composition for stripping
objects of materials vulnerable to corrosion, said
5 composition containing N-methyl-pyrrolidone, potassium
hydroxide and an alcohol having 2 - 3 carbon atoms,
c h a r a c t e r i z e d in containing:
 - A) 0 - 3% by weight of water
 - B) 0.05 - 10% by weight of potassium hydroxide
 - 10 C) 35 - 90% by weight of N-methyl-pyrrolidone, and
 - D) 10 - 60% by weight of an alcohol chosen among
ethanol, n-propanol and i-propanol or mixtures thereof.
2. Composition according to claim 1,
c h a r a c t e r i z e d in that it consists essentially
15 of the ingredients A), B, C), and D) in the ratio A) 0.1% by
weight, B) 1.9% by weight, C) 48% by weight, and D) 50% by
weight.
3. Composition according to claim 1,
c h a r a c t e r i z e d in that in addition to the
20 components A), B), C), and D it contains a flash-point
regulating, essentially neutral component, preferably butyl-
di-glycol.
4. Method for the manufacture of a composition according
to claim 1 for stripping materials vulnerable to corrosion,
25 c h a r a c t e r i z e d in that the alcohol is heated to
at least 50°C, after which the potassium hydroxide is added
under stirring, the stirring being continued until the
potassium hydroxide has been completely dissolved, after
which the N-methyl-pyrrolidone is added under stirring.
- 30 5. Use of the composition according to claim 1 for
stripping objects of metals vulnerable to corrosion by cold-
stripping.
6. Use according to claim 5,
c h a r a c t e r i z e d in that the objects to be
35 stripped are subjected to an aerosol of the composition.



INTERNATIONAL SEARCH REPORT

International Application No PCT/DK 92/00331

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁵		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC5: C 09 D		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	C 09 D	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸		
SE,DK,FI,NO classes as above		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 3551204 (JUSTIN C. BOLGER ET AL.) 29 December 1970, see claim 1 column 2, lines 28-38; column 3, lines 10-15 --	1-6
A	US, A, 3954648 (EDWARD JOHN BELCAK ET AL.) 4 May 1976, see claim 1, column 2, lines 14-15, lines 49-52 --	1-6
A	EP, A1, 0021149 (INTERNATIONAL BUSINESS MACHINES CORPORATION) 7 January 1981, see claims 1, 4-6 --	1-6
P,A	US, A, 5091103 (ALICIA DEAN ET AL.) 25 February 1992, see the abstract, claim 1 -- -----	1-6
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IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
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International Searching Authority		Signature of Authorized Officer
SWEDISH PATENT OFFICE		Barbro Nilsson

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/DK 92/00331

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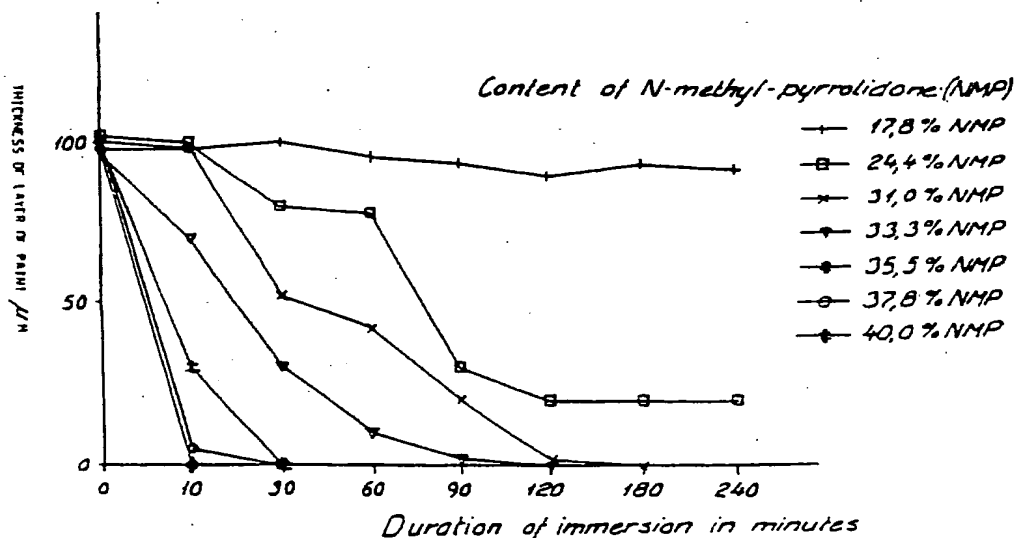
Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3551204	70-12-29	NONE	
US-A- 3954648	76-05-04	DE-A- 2062602 FR-A- 2074058 GB-A- 1291949	71-09-02 71-10-01 72-10-04
EP-A1- 0021149	81-01-07	CA-A- 1124610 JP-C- 1189288 JP-A- 56005899 JP-B- 58021000 US-A- 4276186	82-06-01 84-02-13 81-01-21 83-04-26 81-06-30
US-A- 5091103	92-02-25	WQ-A- 91/17484	91-11-14



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(54) Title: COMPOSITION FOR STRIPPING ENAMELED OR PAINTED SURFACES AND METHOD FOR ITS MANUFACTURE



(57) Abstract

An essentially anhydrous composition for stripping objects of materials vulnerable to corrosion, said composition containing N-methyl-pyrrolidone, potassium hydroxide and an alcohol having 2-3 carbon atoms, contains said components in the following amounts: A) 0-3 % by weight of water, B) 0.05-10 % by weight of potassium hydroxide, C) 35-90 % by weight of N-methyl-pyrrolidone, and D) 10-60 % by weight of an alcohol chosen among ethanol, n-propanol and i-propanol or mixtures thereof. In this way a stripping composition is provided, which is capable of dissolving a considerable number of commonly used types of enamel, which does not corrode aluminium and which does not present any danger to the health of the persons using the composition.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/DK 92/00331

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A	US, A, 3954648 (EDWARD JOHN BELCAK ET AL.) 4 May 1976, see claim 1, column 2, lines 14-15, lines 49-52 --	1-6
A	EP, A1, 0021149 (INTERNATIONAL BUSINESS MACHINES CORPORATION) 7 January 1981, see claims 1, 4-6 --	1-6
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* Special categories of cited documents:¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
30th June 1993	01 -07- 1993	
International Searching Authority	Signature of Authorized Officer	
SWEDISH PATENT OFFICE	Barbro Nilsson	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/DK 92/00331**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 08/01/93. The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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